European Polymer Journal 49 (2013) 768–779

Contents lists available at SciVerse ScienceDirect

European Polymer Journal

journal homepage: www.elsevier.com/locate/europolj

Feature Article

Recent advances in ring-opening polymerization strategies toward α,ω-hydroxy telechelic polyesters and resulting copolymers

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ARTICLE INFO

Article history:
Received 31 August 2012
Received in revised form 10 October 2012
Accepted 11 October 2012
Available online 23 October 2012

Keywords:
Borohydride
Carbonate
(co)Polymers
Ester
Macrodiol
Telechelic

ABSTRACT

α,ω-Hydroxy telechelic polymers, namely macromolecules with reactive hydroxyl end-groups at each chain-end, are industrially highly valuable as building blocks for various ABA or multiblock copolymer architectures. This feature article reviews the different synthetic strategies that we have been developing over the past decade for the preparation of α,ω-hydroxy telechelic polyesters. The ring-opening polymerization (ROP) of several cyclic esters and carbonate, namely ε-caprolactone (CL), β-butyrolactone (BL) or trimethylene carbonate (TMC), catalyzed by intrinsically different systems based on discrete group III metal borohydride complexes, zinc alkoxide compounds generated *in situ*, metallic salts or organocatalysts, directly affords the corresponding difunctionalized hydroxy telechelic poly(ε-caprolactone) (PCL), poly(3-hydroxybutyrate) (PHB) or poly(trimethylene carbonate) (PTMC), PCL–$(OH)_2$, PHB–$(OH)_2$ or PTMC–$(OH)_2$, respectively. Subsequent use of such macrodiols in the polymerization of a co-monomer allows the preparation of unique triblock polyester copolymers. The post-polymerization chemical modification of di-OH functionalized PCLs into the corresponding di-NH_2 or di-Br polymers, followed by the ROP of γ-benzyl-L-glutamate *N*-carboxyanhydride (BLG), or by the radical polymerization of methyl methacrylate (MMA), enables to access to PCL–$PBLG_2$ (PBLG: poly(γ-benzyl-L-glutamate *N*-carboxyanhydride)) and PCL–$PMMA_2$ (PMMA: poly(methyl methacrylate)) triblock copolymers, respectively. Finally, polyaddition of a diamine with the di-(cyclocarbonate) end-functionalized PTMC, derived from PTMC diols, smoothly affords non-isocyanate polyurethanes (NIPUs). The quite different opportunities within reach from α,ω-hydroxy telechelic polyesters, that we have successfully explored, are thus highlighted.

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0014-3057
http://dx.doi.org/10.1016/j.eurpolymj.2012.10.011

1. Introduction

Telechelic polymers are regarded as macromolecules featuring reactive end-groups which have the ability to further promote inter- or intra-molecular bond formation. They provide access to a large range of architectures of which the simplest one remains block copolymers. In particular, ABA triblock copolymers have fostered much industrial interest for the development of thermoplastic elastomers. The topology of the copolymer, the nature, length and sequence distribution of each segment can be easily tuned to meet the industrial specific needs in terms of physical properties [1]. Telechelic polymers featuring controlled molecular characteristics, *i.e.* well-defined and precisely controlled/fine-tuned microstructure, end-group fidelity, predictable and narrow molar mass and dispersity ($Đ_M$ = $\overline{M}w/\overline{M}n$) values, are highly desirable as synthetic building blocks toward more sophisticated unique tailored-made polymer materials. Among the wide variety of the versatile α,ω-telechelic polymers available, hydroxy and carboxylic acid end-functionalized macromolecules have been largely developed since they are commonly involved in polycondensation reaction. Of high significance, hydroxy telechelic polymers are also quite valuable given that they allow the preparation of polyurethanes upon reaction with difunctional isocyanates [1b]. Polymer networks with commercial added-value applications are similarly obtained from the stoichiometric reaction of such telechelic polymers with multifunctional cross-linkers.

Ionic (cationic and anionic), radical and metathesis polymerizations as well as polycondensation, have been used to synthesize telechelic polymers. Of particular relevance to the work described herein is the synthesis of telechelic polyesters by ring-opening polymerization (ROP) of cyclic esters. In the preparation of polyester diols (polyester–$(OH)_2$), whereas post-polymerization chemical modification of a (suitable) pre-polymer enables to end-cap it with the desired OH functions, these functional end-groups can also be directly – and thus more elegantly – introduced during the initiation or by transfer reactions. Indeed, use of a difunctional metallic initiator allows the synthesis of polyester–$(OH)_2$, as demonstrated from aluminum or tin dialkoxide complexes; however, the relatively high concentration of initiator generally required remains a flaw especially with low-molar mass polymers [1,2]. Alternatively, use of a chain transfer agent, such as in the so-called "immortal" ROP (iROP), allows to significantly lower the initiator concentration; when the transfer agent is a diol, dihydroxy end-capped polymers are thus readily formed [3,4].

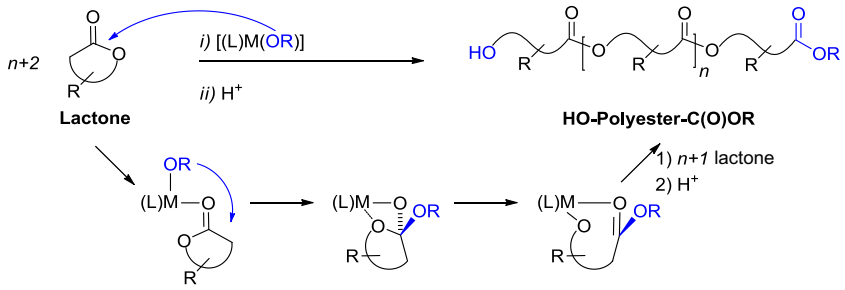
We have been designing α,ω-dihydroxytelechelic polyesters following two strategies: (1) the direct synthesis of diOH-end functionalized polyesters triggered during the initiation upon using suitable catalysts, namely discrete metal borohydride complexes, and (2) the iROP of a cyclic monomer using a diol as transfer agent in association with a metallo-organic, metallic or organic catalyst. Thus, hydroxy-difunctionalized poly(ε-caprolactone) (PCL), poly(β-butyrolactone) (PHB) or poly(trimethylene carbonate) (PTMC), PCL–$(OH)_2$, PHB–$(OH)_2$ or PTMC–$(OH)_2$, respectively, have been prepared. The main motivation in these studies was to establish novel synthetic routes toward polyester diols, next offering further opportunities in macromolecular engineering.

Post-polymerization chemical modification of a polymer chain-end(s) into (an)other functional group(s) is a classical approach to the preparation of copolymers for which the (at least two) monomers involved cannot be copolymerized via the same polymerization route. Thus, these polyesters-diols, subsequently chemically modified into the diamino, dibromo or di(cyclocarbonate) analogues, have next been used as macroinitiators either in the ROP of γ-benzyl-L-glutamate *N*-carboxyanhydride (BLG), in the radical polymerization of methyl methacrylate (MMA), or in the polycondensation with a diamine, offering the corresponding PCL–$PBLG_2$ (PBLG: poly(γ-benzyl-L-glutamate *N*-carboxyanhydride)), PCL–$PMMA_2$ (PMMA: poly(methyl methacrylate)) triblock copolymers, or the poly(carbonate urethane)s, respectively. A variety of (co)polymers with different outcomes have thus become accessible. Such biocompatible and (bio)degradable (co)polymers are of upmost importance for biomedical applications, food packaging, disposable items as well as commodity plastics, all the more when they are renewable resource polymers [5,6].

This contribution is an account of our results from the past decade on the synthesis of α,ω-dihydroxy telechelic polyesters and on their valorization in macromolecular engineering toward the synthesis of ABA triblock copolyesters with peptide, methacrylate or urethane segments, highlighting the originality of the strategies established and their overall reward.

2. Synthesis of α,ω-dihydroxy telechelic polyesters

The ROP of cyclic esters has been widely developed through a coordination-insertion mechanism promoted by coordination complexes of the type [(L)M–X] (L = supporting ligand(s); M = main group, transition or rare earth



Scheme 1. ROP of a model lactone initiated by a metal alkoxide complex [(L)M–OR]: synthesis of α-hydroxy, ω-alkoxy ester telechelic polyester.

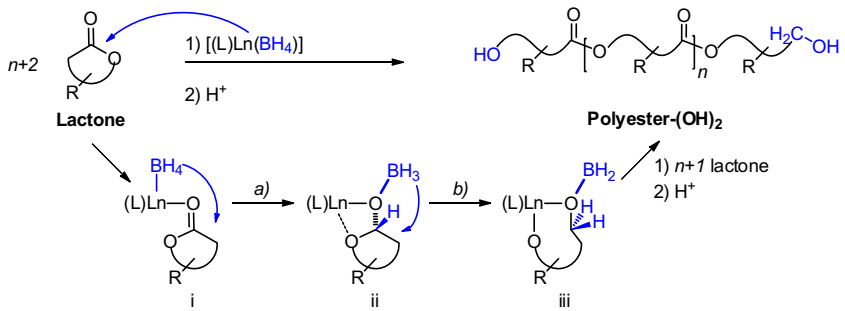
metal; X = active function: hydride, alkyl, aryl, amide, and alkoxide) [7,8]. The nature of the metal center M, the ancillary ligand(s) L, and the M–X bond, as well as the number of active functions X, are essential in dictating the ROP mechanism, the control of the ROP and of the macromolecular features (especially molar mass, dispersity and tacticity), and ultimately the thermal and mechanical properties of the resulting polymer. Alkoxide initiators (X = OR), which remain the most commonly used, typically afford the corresponding α-hydroxy, ω-alkoxy ester telechelic polyesters upon oxygen–acyl bond rupture of the monomer, as exemplified in Scheme 1 for the ROP of a model lactone [1b,7,8]. Whereas the alkoxy ester end-group originates from the alkoxide ligand flanked onto the metal center, the hydroxyl terminal function is formed upon hydrolysis of the active metal–oxygen bond during the termination/deactivation step [7–9].

2.1. Synthesis of α,ω-dihydroxy telechelic poly(ε-caprolactone) and poly(β-butyrolactone) from discrete group III metal borohydride complexes

Polymer-diols are, as just discussed, not accessible from the ROP of a cyclic ester promoted by either alkoxide initiators or other hydride, alkyl/aryl or amide precursors [7,8a]. In comparison, we have demonstrated that the ROP of lactones such as ε-caprolactone (CL) [8a,10–12] or β-butyrolactone (BL) [13], initiated by a discrete group III (M = Ln = rare earth) metal complex bearing a borohydride ligand (X = BH_4; latest and recently unveiled active function in metal-catalyzed ROP of cyclic esters), directly affords the corresponding α,ω-dihydroxy telechelic polyesters, as depicted in Scheme 2. The original idea in evaluating borohydride rare earth complexes in the ROP of cyclic esters – and methacrylates (*vide infra*) – was to possibly gain unprecedented reactivity arising from the hydridic nature of the bond between the metal and the boron centers, which features bridging hydrogen atoms [14]. Indeed, rare earth hydride complexes had previously been shown by Yasuda as unusually highly efficient catalysts in the polymerization of polar monomers, in particular CL and methylmethacrylate [14,15].

Initially investigated from the most easily synthetically accessible and simpler homoleptic rare earth metal complexes, [$Ln(BH_4)_3(THF)_3$] with Ln = La, Nd, Sm [16], the following ROP of cyclic esters studies involved single site (monoborohydride) as well as bisborohydride complexes, the latter two providing, thanks to their ancillary ligand(s) (L(s)), more crystallinity and solubility to the active species (thus enabling their complete characterization and a better understanding of the ROP mechanism) as well as potential site(s) of interaction with the liberated BH_3 species (*vide infra*).

The first efforts were essentially focused on CL, a monomer easily prone to undergo ROP [7a]. Extensive investigations on the ROP of CL first unveiled and demonstrated the possibility to synthesize PCL-$(OH)_2$ from such borohydride catalysts. Both experimental and mechanistic insights were thoroughly evidenced using [$Ln(BH_4)_3(THF)_3$] with Ln = La, Nd, Sm, and in particular the bis(pentamethylcyclopentadienyl) samarium complex, [$(\eta^5\text{–}C_5Me_5)_2$-$Sm(BH_4)(THF)$]. As the first single site borohydride derivative involved in the ROP of a cyclic ester, this latter catalyst, on the one hand, helped in the identification of several reaction intermediates, and on the other hand promoted slower and therefore better controlled ROP process



Scheme 2. ROP of a model lactone initiated by a rare earth metal borohydride complex [(L)Ln(BH_4)]: synthesis of α,ω-dihydroxy telechelic polyester.

(less unwanted side reactions observed) of CL, in comparison to $[Ln(BH_4)_3(THF)_3]$ [8a,10]. Eventually, it then opened up the way to the ROP of polar monomers promoted by heteroleptic post-metallocene borohydride catalysts. Thus, the bis(phosphinimino)methanide borohydride complexes $[\{CH(PPh_2N(SiMe_3))_2\}La(BH_4)_2(THF)]$ and $[\{CH(PPh_2N(SiMe_3))_2\}Ln(BH_4)_2]$ (Ln = Y, Lu) developed by Roesky and co-workers [17], were shown to be efficient in the controlled and living ROP of CL [11]. Noteworthy, such catalysts afforded, thank to the favorable stereoelectronic contribution of the surrounding ligand, the narrowest polymer dispersity ($1.06 < Đ_M < 1.11$) ever obtained in a controlled ROP of a cyclic ester -in this case CL ($\overline{Mn} \leq 22,400\,g\,mol^{-1}$) – promoted by a rare earth borohydride derivative [11,14]. This behavior also highlighted the significant contribution of the ancillary bis(phosphinimino)methanide ligand in the overall ROP mechanism, as further supported by DFT studies (*vide infra*) [11]. Also, aminopyridinato (Ap*H = (2,6-diisopropyl-phenyl)-[6-(2,4,6-triisopropyl-phenyl)-pyridin-2-yl]-amine) borohydride complexes of divalent as well as trivalent lanthanides, generated *in situ* from the reaction of the corresponding halides $[(Ap^*)LaBr_2(THF)_3]$, $[(Ap^*)YbI(THF)_2]$ or $[(Ap^*)LuCl_2(THF)_2]$ [18] with $NaBH_4$, as developed in collaboration with Kempe and co-workers, smoothly afforded the PCL-$(OH)_2$ from the controlled ROP of CL [12]. This latter strategy thus demonstrated, for the first time, that prior (sometimes difficult or inaccessible) isolation of the borohydride precursor can be easily circumvented upon its *in situ* preparation. Also, it allowed evaluation of the effect of diverse halide precursors (Cl *vs.* Br *vs.* I) as well as distinct rare earth metal oxidation state (+II *vs.* +III). The larger trivalent lanthanum bromide based initiating system $[(Ap^*)LaBr_2(THF)_3]/NaBH_4$ afforded the best defined PCLs (best agreement between $\overline{Mn}$ values determined by SEC and the expected ones; narrowest $Đ_M \approx 1.45$), while the smaller divalent ytterbium iodide precursor $[(Ap^*)YbI(THF)_2]$ led to higher molar mass PCLs ($\overline{Mn} \leq 47,500\,g\,mol^{-1}$, $Đ_M \approx 1.56$) and the trivalent lutetium chloride ranged in between. Noteworthy, no oxidation of the rare earth metal center was observed during these ROPs [12].

More recent results have demonstrated the activity of the homoleptic complexes $[Ln(BH_4)_3(THF)_3]$ with Ln = La, Nd, Sm, in the controlled ROP of the higher strained four-membered ring β-lactone, BL, similarly affording poly(3-hydroxybutyrate) diols (PHB-$(OH)_2$) [13]. The lower reactivity of the catalysts toward the ROP of BL (100 BL units converted in 23 h in toluene at 25 °C) [13] *vs.* that of CL (100 CL units converted within 10 or 15 min in CH_2Cl_2/Toluene (30/70 v/*v*) or THF, respectively) [10a,10c], remained in agreement with the established reluctance of this smaller monomer to undergo ROP, in comparison to the significantly more reactive related higher lactones [19]. Well-defined low molar mass PHBs were thus synthesized ($\overline{Mn} \leq 10,000\,g\,mol^{-1}$, $1.02 < Đ_M < 1.10$).

Most generally, the molar mass of all these polyester-diols thus synthesized remained below $\overline{Mn} = 50,000\,g\,mol^{-1}$ [8a,10–14]; yet, higher molar mass were definitely not the main objective of all these studies which were rather focused on mechanistic investigations. Also, ROP usually proceeded in a "living" and controlled manner, with one growing polymer chain being formed per Ln–BH_4 entity.

Comprehensive in depth studies on the reaction mechanism, based on ^1H, ^{13}C, ^{11}B, ^{31}P, 2D ^1H-^1H COSY, HMQC, and HSQC NMR, FTIR, MALDI-ToF mass spectrometry and elemental analyses of the various intermediates (especially **i** and **iii**) and final polymer, have led to the proposed general mechanism depicted Scheme 2 for $[Ln(BH_4)_3(THF)_3]$. Initially, CL displaces the THF molecules to coordinate to the [Ln–BH_4] complex through the carbonyl group thus forming **i**. Then, upon insertion of this first CL molecule into the Ln–HBH_3 bond, the hydride transfer to the adjacent carbonyl carbon of the lactone and the BH_3 transfer to the formally anionic oxygen lead to **ii** moiety (Scheme 2-step a). Ring-opening via oxygen–acyl bond cleavage subsequently takes place in the penultimate step of the initiation process, with a second hydride transfer onto the same carbon affording **iii**, thus featuring a fully reduced carbonyl moiety (Scheme 2-step b). Further incoming monomer units subsequently ring-open polymerize following this same coordination-insertion route until the propagation is terminated upon protonolysis of the active polymeryl chain, *i.e.* hydrolysis of the Ln–O bond and of the –OBH_2 moiety, thereby offering the α,ω-dihydroxy telechelic polyester. In contrast to the metal alkoxide mediated ROP of a cyclic ester which forms α-hydroxy, ω-alkoxy ester telechelic polyester (Scheme 1), the originality of the ROP of a lactone promoted by a metal borohydride derivative lies in the monomer carbonyl reduction induced by the BH_3 group which directly provides polyester-diols [8a,10–14].

The relevant contribution of DFT studies to the overall ROP of cyclic esters catalyzed by homoleptic and heteroleptic rare earth borohydride complexes has been highlighted throughout various investigations in collaboration with Maron and co-workers [11,13,20]. Differences between the hydride and borohydride as well as between metallocene and non-metallocene borohydride precursors, modeled especially by $[(C_5H_5)_2Eu(X)]$ with X = H, BH_4, $[\{CH(PMe_2NSiH_3)_2\}Y(BH_4)_2]$ and $[(N_2NN')Eu(BH_4)]$ (N_2NN' = (2-C_5H_4N)$CH_2(CH_2CH_2NMe)_2$ as developed by Mountford and co-workers [21]), especially aided this topical and important field of research. In particular, efforts to better understand the thermodynamics and kinetics of the initiation step, with the coordination-insertion of the real first monomer molecule (Scheme 2-steps a and b), have undoubtedly enabled to strongly computationally support the formation of the alkoxide–borate intermediate **iii**, ultimately unambiguously leading to α,ω-dihydroxy telechelic polyesters, as obtained experimentally [8a,10–13,20]. Furthermore, the significant contribution of the supporting ligand has been unveiled with the careful comparative investigations of the two successive B–H activations of BH_4^- (Scheme 2-steps a and b) leading to the borate **iii**, involving metallocene $[(C_5H_5)_2Eu(BH_4)]$ or post-metallocene $[\{CH(PMe_2NSiH_3)_2\}Y(BH_4)_2]$ and $[(N_2NN')Eu(BH_4)]$ derivatives. In particular, an unprecedented first B–H activation (Scheme 2-step a) achieved in two steps, was established from the computed free energy profile of the reaction of CL with $[\{CH(PMe_2NSiH_3)_2\}Y(BH_4)_2]$ [11]. This was opposed to the unique step involved with the monoborohydride metallocene, $[(C_5H_5)_2$-

Eu(BH_4)], and non-metallocene [(N_2NN')Eu(BH_4)], complexes [20]. In the case of [{CH(PMe_2NSiH_3)$_2$}Y(BH_4)$_2$], in this first B-H activation, the nucleophilic attack of one hydride onto the carbon atom of the ketone takes place along with the decoordination of BH_4^- from yttrium. Subsequently, the original trapping of the liberated BH_3 moiety by the oxygen atom of the ketone then occurs (while the second BH_4^- ligand remains bonded to the yttrium center), leading to the formation of the borate intermediate (analogous to **ii**). This unique behavior results not only from the presence of two BH_4 groups in [{CH(PMe_2NSiH_3)$_2$}Y(BH_4)$_2$], but also from the beneficial electron-donating ability of the bis(phosphinimino)methanide ligand [11]. The second subsequent B-H activation (Scheme 2-step b), classical for a rare earth borohydride catalyst, involves the ring-opening of the monomer, induced by the hydrogen transfer from the trapped BH_3 to the ketonic carbon (the same as in the first step). Upon final hydrolysis (termination deactivation), the ketone is then reduced, affording α,ω-dihydroxy telechelic polyesters, in agreement with the experimental findings [11].

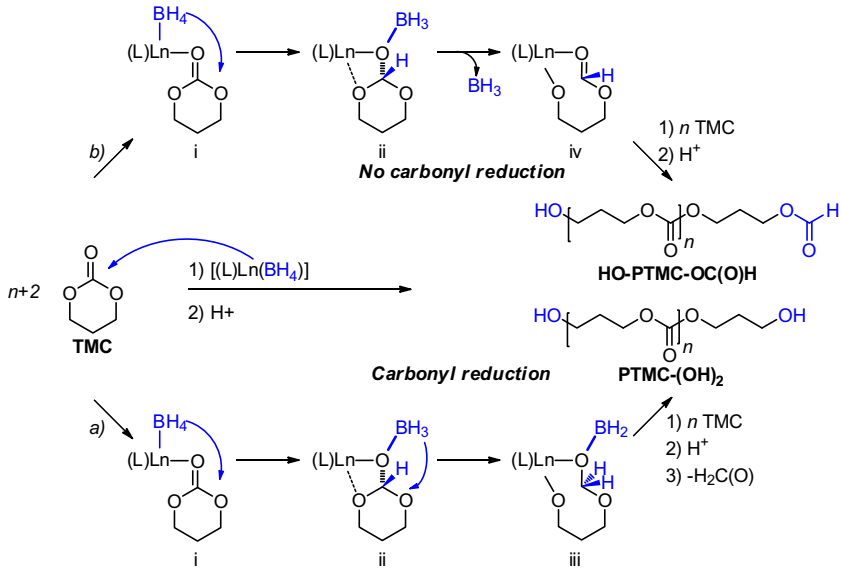
Our initial work on the ROP of ε-caprolactone from such rare earth borohydride complexes pioneered the research in the ROP of polar monomers from such BH_4-initiators [14]. The general ROP approach is common to all lactones and dilactones as later on reported with β-butyrolactone, δ-valerolactone, ω-pentadecalactone as well as lactides [13,22]. However, the ROP of a cyclic carbonate initiated from such rare earth borohydride species does not systematically afford the polycarbonate diol.

2.2. Synthesis of α,ω-dihydroxy telechelic poly(trimethylene carbonate) from discrete group III metal borohydride complexes

In comparison to CL, the ROP of trimethylene carbonate (TMC) catalyzed by rare earth borohydride precursors has been much less investigated [23]. The few borohydride complexes evaluated, namely [Sm(BH_4)$_3$(THF)$_3$][23a], [{CH($PPh_2N(SiMe_3)$)$_2$}La(BH_4)$_2$(THF)] and [{CH(PPh_2-$N(SiMe_3)$)$_2$}Ln(BH_4)$_2$] (Ln = Y, Lu) [23b], successfully polymerized TMC in a controlled and "living" manner affording linear PTMCs.

The trisborohydride samarium precursor [Sm(BH_4)$_3$-(THF)$_3$] afforded α-hydroxy, ω-formate telechelic PTMCs, as determined experimentally from detailed ^{1}H, ^{13}C, ^{1}H-^{1}H COSY, ^{1}H-^{13}C HMQC NMR and MALDI-ToF mass spectrometry analyses. Indeed, in this case, in contrast to the ROP of CL, the BH_3 moiety does not reduce the adjacent carbonyl carbon of the carbonate group. Elimination of BH_3, prior or post-termination/deactivation, leads to the formation of the heterofunctionalized PTMC (Scheme 3b) [23a].

The post-metallocene rare earth complexes [{CH(PPh_2-$N(SiMe_3)$)$_2$}Ln(BH_4)$_2$(THF)$_x$] (Ln = La (x = 1), Y and Lu (x = 0)), similarly gave, based on experimental evidences, this same hetero(hydroxy-formate) functionalized PTMC [23b]. However, formation of the related α,ω-dihydroxy telechelic PTMC, which could not be ruled out from experimental data (both HO–PTMC–OC(O)H and PTMC–$(OH)_2$ display a common signal corresponding to the terminal methylene hydrogens –CH_2OH), was also evidenced from DFT calculations. Observation of these two types of functionalized PTMCs was supported by two energetically (thermodynamically and kinetically) favorable and alike reaction pathways. These feasible computed routes, although very close in energy, yet predicted the slightly preferred formation of the α-hydroxy, ω-formate telechelic PTMCs [23b]. The polycarbonate diol was obtained following the carbonyl reduction pathway, upon ultimate formaldehyde elimination from the unstable hemiacetal end-functionalized polymer derived from **iii** (Scheme 3a). Noteworthy, in the HO–PTMC–OC(O)H formation pathway, the significant contribution of the bis(phosphinimi-



Scheme 3. ROP of TMC initiated by a rare earth metal borohydride complex [(L)Ln(BH_4)]: synthesis of α,ω-dihydroxy telechelic and α-hydroxy, ω-formate telechelic PTMC.

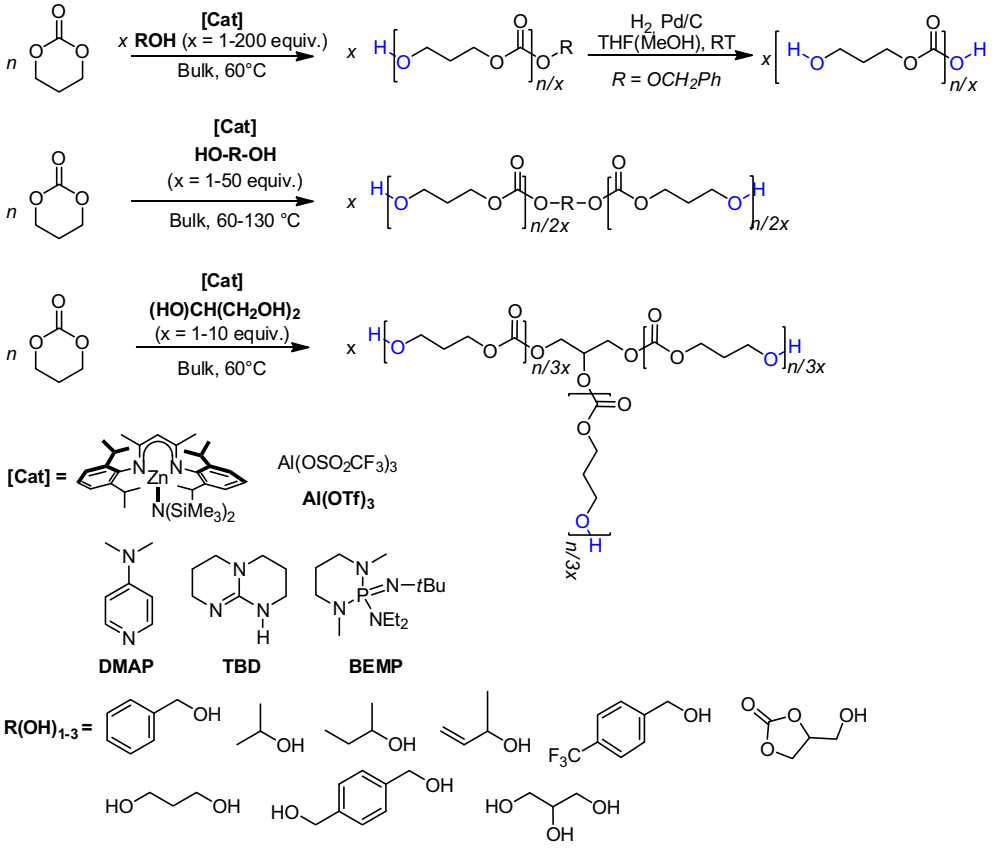
no)methanide ligand in trapping, through the nitrogen atom, the BH_3 moiety liberated prior to the formation of **iv**, was established from these calculations, in line with its behavior in the polymerization of butadiene as supported by X-ray analysis [24].

2.3. Synthesis of α,ω-dihydroxy telechelic poly(trimethylene carbonate) from bicomponent catalyst systems

Another synthetic route toward the preparation of α,ω-hydroxy telechelic PTMC relies on the "immortal" ROP (iROP) of TMC promoted by bi-component catalyst systems associating either a metallo-organic, a simple metallic salt or an organic compound to a protic source, typically an alcohol, acting both as a co-initiator and a chain transfer agent [3]. In particular, a discrete {β-diiminate}zinc amido complex [(BDI*i*Pr)Zn($N(SiMe_3)_2$)] ((BDI*i*Pr) = 2-((2,6-diisopropylphenyl)amido)-4-((2,6-diisopropylphenyl)-imino)-2-pentene], metal triflates such as $Al(OTf)_3$, as well as guanidine (1.5.7-triazabicyclo-[4.4.0]dec-5-ene; TBD), amine (4-*N*,*N*-dimethylaminopyridine; DMAP) or phosphazene (2-*tert*-butylimino-2-diethylamino-1,3-dimethylperhydro-1,3,2-diazaphosphorine; BEMP) bases, have been successfully used with several alcohols [25]. While the use of a monoalcohol (typically BnOH, *i*PrOH, glycerol carbonate) led to α-hydroxy, ω-alkoxy carbonate telechelic polycarbonate, diols or higher alcohols (typically 1,3-propanediol, 1,4-benzenedimethanol or glycerol) afforded linear or star-shaped α,ω-hydroxy telechelic PTMCs (Scheme 4) [3,25]. Remarkably, high activities and productivities (in regard of reported literature data) have been achieved within controlled "living" iROP processes, affording well-defined (as evidenced by NMR and MALDI–ToF analyses) high molar mass PTMC diols ($2000 \leq \overline{M}n \leq 109,500\,g\,mol^{-1}$, $Đ_M < 1.80$) [25]. As many as 50 polymeryl chains could be grown from a unique metal center upon raising the initial monomer loading up to 50,000 equiv., thus enabling to lower the initial metal catalyst content down to 20 ppm [25c]. Note that this approach has been extended to the preparation of linear α,ω-dihydroxy functionalized poly(lactide) as well [25c]. Finally, PTMC–$(OH)_2$ were also alternatively synthesized upon hydrogenolysis of the preformed benzyloxy-terminated PTMC (Scheme 4) [25c].

3. α,ω-Dihydroxy telechelic polyesters in macromolecular engineering: toward original copolymers

One possible outcome of hydroxy telechelic polyesters is to use these as macro-ols in the ROP of cyclic esters toward the synthesis of copolymers. The PTMC diols just mentioned above, made from the iROP of TMC (Scheme 4), have been successfully used as macro-alcohols in the



Scheme 4. "Immortal" ROP of TMC using bicomponent catalyst/alcohol systems: synthesis of α,ω-dihydroxy telechelic PTMC.

synthesis of polycarbonate/polyester copolymers such as PLLA-*b*-PTMC-*b*-PLLA (PLLA = poly(L-lactide)) [26a]. Typically, the same catalyst systems as depicted Scheme 4 have been used in this study. The control of the length/molar mass of the PTMC segment within the PLLA backbone has enabled to favorably tune the thermo-mechanical properties of the resulting polymer material [26a,27]. This latter approach has also been followed for the preparation of new copolymers derived from TMC and other six-membered cyclic carbonates [26b]. Similarly, α-hydroxy, ω-alkoxy ester telechelic PTMCs (Scheme 4) can afford the corresponding diblocks copolymers PTMC-*b*-PLLA and PTMC-*b*-Polycarbonate, thus providing original copolymers [26,27].

The most significant advantage of using rare earth borohydride complexes as catalysts in the ROP of cyclic esters, inherently to the unique reactivity of the BH_4^- ligand itself [14], is the resulting direct (no additional chemical modification step required) synthesis of α,ω-dihydroxy telechelic polyesters/polycarbonates (Schemes 2 and 3). Also, hydroxyl groups are quite reactive further offering a large range of chemical opportunities. We thus next exploited such dihydroxy telechelic polymers in macromolecular engineering.

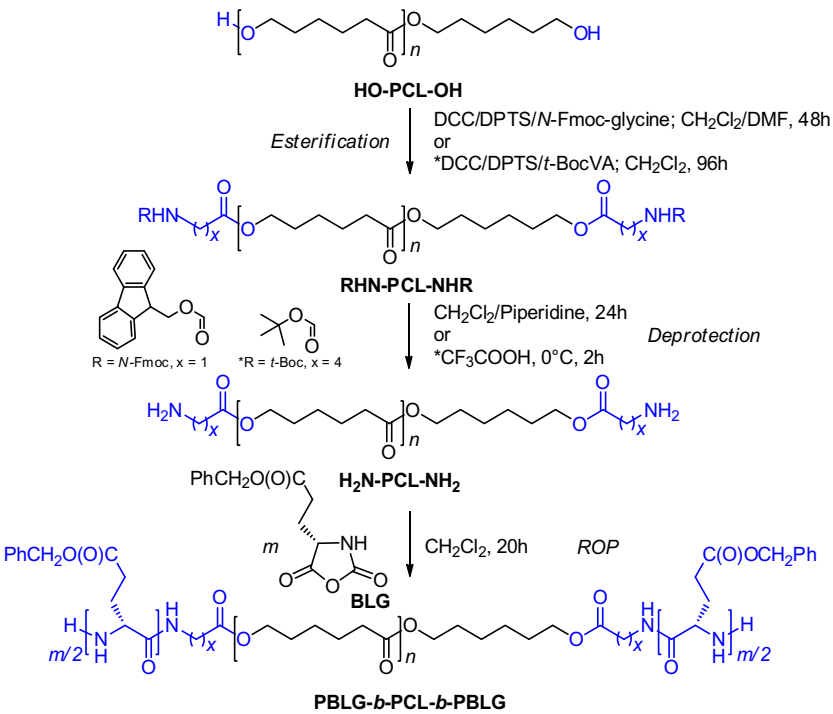
Following the chemical modification of the OH functions into other reactive groups, specifically selected for their ability to undergo, in particular, a different polymerization process (non cyclic ester ROP) of a second distinct (non cyclic ester) monomer, original (multi-)block copolymers otherwise not so straightforwardly obtained, could thus be prepared. Changing the terminal OH functions into primary amino, α-bromoester or cyclocarbonate groups, one can further initiate the ROP of an α-amino acid NCA, the radical polymerization of a methacrylate, or a polycondensation reaction with a diamine, respectively. This represents an alternative strategy to the unsuccessful (direct) copolymerization of such mechanistically incompatible monomers.

Remarkably, the strategies described thereafter, developed from either the mono- or the di-hydroxyfunctionalized polymers, allowed to access to analogous diblock and triblock polyester/polypeptide, polymethacrylate, polyurethane architectures. In this regard, in light of the state of the art, our general approach thus appears quite unique.

3.1. Chemical modification of α,ω-dihydroxy telechelic polyesters into α,ω-diamino telechelic macroinitiators for the synthesis of polyester/polypeptide copolymers

Both terminal hydroxyl functions of the poly(ε-caprolactone) diol, PCL–$(OH)_2$, have thus been chemically modified into the corresponding diamino analogues, PCL–$(NH_2)_2$. Subsequently, polyester/polypeptide block copolymers have been synthesized using these diamino end-functionalized polyesters as macroinitiators in the ROP of γ-benzyl-L-glutamate *N*-carboxyanhydride (BLG; Scheme 5) [28].

Indeed, the quantitative esterification of the hydroxy-terminated PCL upon its condensation with an *N*-protected amino acid (*N*-(9-fluorenylmethoxycarbonyl)-glycine (*N*-Fmoc-glycine) or 5-(*tert*-butoxycarbonylamino)valeric acid (*t*-Boc-VA)) using 4-(dimethylamino)pyridine toluenesulfonate (DPTS) and dicyclohexylcarbodiimide (DCC) as catalysts, afforded the corresponding secondary amine functionalized PCL. Quantitative *t*-Boc or *N*-Fmoc deprotection under mild conditions subsequently gave the corresponding α,ω-diamino telechelic PCL, PCL–$(NH_2)_2$. The



Scheme 5. Synthesis of PBLG-*b*-PCL-*b*-PBLG from α,ω-dihydroxy telechelic PCL.

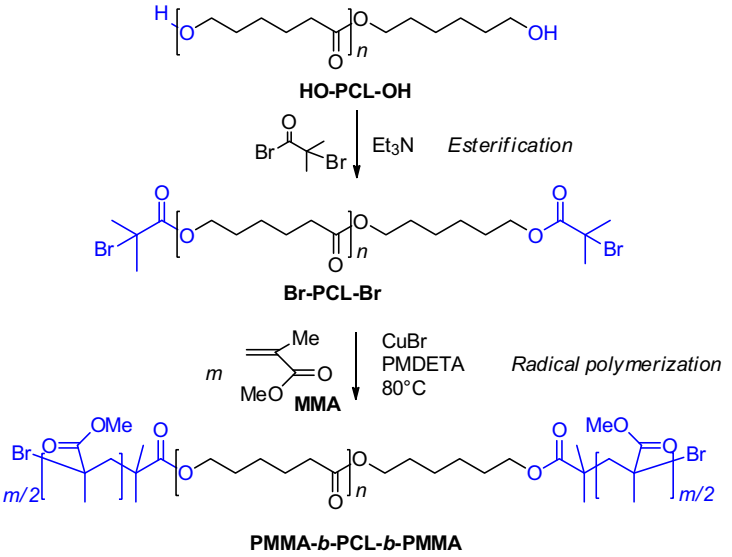
ROP of BLG from this diamino macroinitiator finally afforded the related well-defined ($\overline{M}n_{SEC} \approx \overline{M}n_{NMR} \approx \overline{M}n_{theo}$; $1.1 < Đ_M < 1.4$) triblock copolymers PBLG-*b*-PCL-*b*-PBLG (PBLG: poly(γ-benzyl-L-glutamate *N*-carboxyanhydride); $10,800 < \overline{M}n_{NMR} < 72,600\,g\,mol^{-1}$; Scheme 5). Note that following this same approach, the analogous diblock copolymers PCL-*b*-PBLG ($13,200 < \overline{M}n_{NMR} < 28,900\,g\,mol^{-1}$; $Đ_M \approx 1.2$) were similarly prepared from the mono-hydroxy terminated polymer, HO–PCL–O^{i}Pr (synthesized from [La(O^{i}Pr)$_3$] [8a], refer to Scheme 1) [28]. While both PCL and PBLG enriched diblock copolymers were prepared (25:46 < PBLG:PCL < 100:46), triblock copolymers always featured similar-to-larger content of the polypeptide segment (20:23 < PBLG:PCL < 300:64). These various steps were carefully monitored and supported by ^{1}H and ^{13}C NMR and SEC analyses. In particular, the disappearance of the typical –C*H*$_2$OH initial signal [29a], followed by the appearance and next disappearance of the resonances characteristic of the *N*-Fmoc or *t*-Boc moiety, were carefully examined.

The chemical composition of the PCL/PBLG block copolymers was determined and confirmed by NMR, FTIR and DSC analyses. In particular, alongside the typical signals corresponding to the backbone hydrogen atoms of both the polyester and the polypeptide blocks, the characteristic NH$_2$C*H*$_2$C(O) triplet [29b] observed in the ^{1}H NMR spectra confirmed the growth of the polypeptide segment from primary amines at both chain ends of the prepolymer. FTIR spectra clearly evidenced the typical absorption bands of each block [30], thus corroborating the formation of the polypeptide block from the initial polyester segment. Also, the characteristic thermal transitions temperature(s) of each block (PCL: $Tg \approx -53$ °C, $Tm \approx 57$ °C; PBLG: 103–122 °C = irreversible transition corresponding to an irreversible change from a seven-residue two-turn (7/2) to an 18/5 α-helical conformation) were recorded by differential scanning calorimetry (DSC). Following a similar approach, the related PTMC-*b*-PBLG diblock copolymers ($4700 < \overline{M}n_{NMR} < 12,100\,g\,mol^{-1}$; $Đ_M \approx 1.2$) were subsequently synthesized [31].

3.2. Chemical modification of α,ω-dihydroxy telechelic polyesters into α,ω-di(α-bromoester) telechelic macroinitiators for the synthesis of polyester/polymethacrylate copolymers

Given the poor reactivity of the rare earth borohydride complexes [Ln(BH$_4$)$_3$(THF)$_3$] (Ln = La, Nd, Sm) or [{CH(PPh$_2$N(SiMe$_3$))$_2$}Ln(BH$_4$)$_2$(THF)$_x$] (Ln = La (x = 1), Y and Lu (x = 0)), in the polymerization of methylmethacrylate (MMA), especially their failure to provide a controlled process, the sequential copolymerization of CL and MMA aimed at the preparation of well-defined PCL/PMMA block copolymers, could not be achieved from such catalysts [32]. Therefore, a suitable route to such copolymers was sought. Thus, the post-polymerization chemical modification of both OH groups of α,ω-dihydroxy telechelic PCL into the corresponding di(α-bromoester) end-functionalized polyester, was developed, aiming at the synthesis of polyester/polymethacrylate copolymers upon subsequent radical polymerization of MMA (Scheme 6) [33].

The quantitative esterification of the hydroxyl end-groups of PCL–(OH)$_2$ using 2-bromoisobutyryl bromide in presence of Et$_3$N afforded the corresponding PCL–Br$_2$, as confirmed by ^{1}H and ^{13}C NMR analyses (Scheme 6). The integrity of the backbone chain was maintained as evidenced by NMR and SEC analyses. Such di(α bromoester)-PCL then smoothly behaved as macroinitiators for the controlled radical polymerization of MMA, using CuBr in presence of the multidentate ligand pentamethyldiethylenetriamine (PMDETA) used as a catalyst, to afford PMMA-*b*-PCL-*b*-PMMA (up to 77% MMA conversion; $(14,600 < \overline{M}n_{NMR} \approx \overline{M}n_{theo} < 64,200\,g\,mol^{-1}$; $Đ_M \approx 1.35)$. Note that correspondingly, analogous diblock copolymers PCL-*b*-PMMA ($11,260 < \overline{M}n_{NMR} \approx \overline{M}n_{SEC} \approx \overline{M}n_{theo} < 29,100\,g\,mol^{-1}$; $Đ_M \approx 1.2$) were prepared from the mono-hydroxy terminated polymer, HO–PCL–O^{i}Pr (synthesized



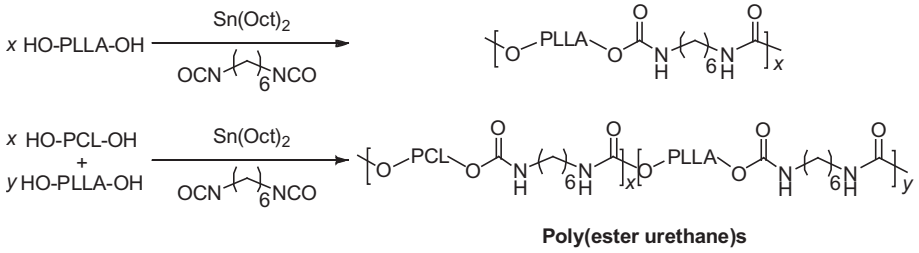
Scheme 6. Synthesis of PMMA-*b*-PCL-*b*-PMMA from α,ω-dihydroxy telechelic PCL.

from [La(O^{i}Pr)$_3$] [8a]) [33]. The growth of the MMA segment(s) upon polymerization featured a linear increase with the $[MMA]_0/[PCL–Br_2]_0$, consistent with a "living" process [33].

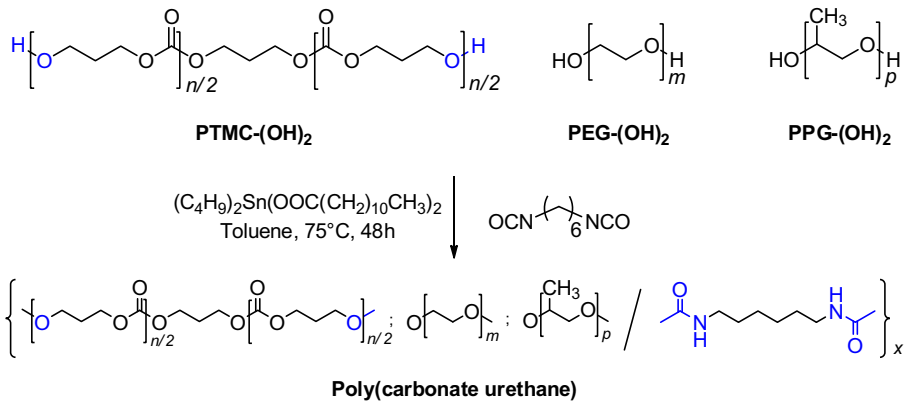
The chemical composition and microstructure of the PCL/PMMA copolymers, as determined by ^{1}H and ^{13}C NMR, SEC and DSC analyses, confirmed their blocky nature. Successive disappearance of the –C*H*$_2$OH [29a], appearance and next disappearance of –C*Me*$_2$Br [29c] NMR signals along with the ultimate observation of the characteristic MMA signals (in particular –C(O)OC*H*$_3$ [29d]), supported the quantitative end-functionalization of the PCL diols, and the successful MMA propagation at both α-bromoester chain ends, respectively. While the experimental molar mass values of the diblock copolymers were in agreement with the calculated ones ($\overline{M}n_{NMR} \approx \overline{M}n_{SEC} \approx \overline{M}n_{theo}$), the larger PMMA segments in the triblock structures induced lower molar mass data as determined by SEC, in comparison to the similar values of $\overline{M}n_{NMR}$ and $\overline{M}n_{theo}$. All these block copolymers featured dispersity values in the range $Đ_M = 1.6$ with rather syndiotactic PMMA segments (mm/mr/rr ≈ 7/34/59). The composition of the diblock PCL-*b*-PMMA copolymers varied from lactone rich (up to 80%) to methacrylate rich (up to 67%) type, whereas the composition of the prepared triblock PMMA-*b*-PCL-*b*-PMMA remained richer (at least twice as much; up to 89%) in methacrylate segments [33]. The thermograms of the diblock and triblock copolymers measured by DSC highlighted that both the ratio of PMMA to PCL and the length of each block, in combination with the intrinsic crystallinity of each type of polymer, greatly influenced the thermal behavior of the copolymers. Diblock copolymers exhibited (only) a T_m at 50–60 °C corresponding to the PCL segment, which was shifted to 52–53 °C in the triblock, thus highlighting structural differences between the two architectures. The T_g of the MMA segment(s) could only be observed (108 °C) in the methacrylate-enriched triblock copolymers PMMA$_{258}$-*b*-PCL$_{109}$-*b*-PMMA$_{258}$.

3.3. Chemical modification of α,ω-dihydroxy telechelic polycarbonates into α,ω-di(cyclocarbonate) telechelic macroinitiators for the synthesis of polycarbonate/polyurethane copolymers: toward Non-Isocyanate Poly(Urethane)s (NIPUs)

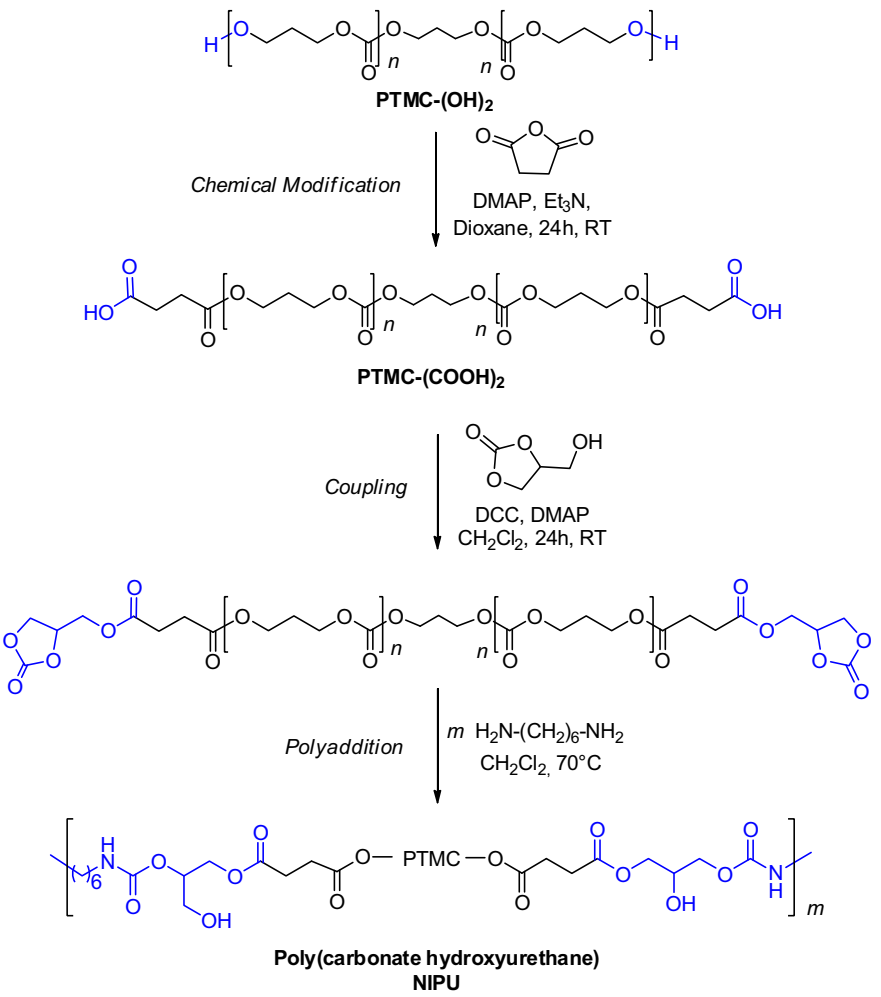
The most common and industrially attractive valorization of α,ω-dihydroxy telechelic polymers remains intended toward the preparation of polyurethanes [1]. The reactive polyester OH chain end-groups can directly undergo chain extension upon polycondensation with a diisocyanate. This was exemplified by Nakayama and Shiono and co-workers with the formation of poly(ester urethane)s from PLLA–(OH)$_2$, or from a mixture of PCL–(OH)$_2$ with PLLA–(OH)$_2$, and 1,6-hexamethylene diisocyanate (Scheme 7) [34]. Lately, the PTMC-diol has been successfully valorized in the synthesis of polyurethanes according to such a "classical" approach (Scheme 8) [35]. The random coupling of PTMC–(OH)$_2$, PEG–(OH)$_2$, (PEG = poly(ethylene glycol)) and PPG–(OH)$_2$ (PPG = poly(propylene glycol)), catalyzed by dibutyltin dilaurate in the presence of 1,6-



Scheme 7. Synthesis of poly(ester urethane)s from α,ω-dihydroxy telechelic polyesters [34].



Scheme 8. Synthesis of poly(carbonate urethane)s from α,ω-dihydroxy telechelic PTMC.



Scheme 9. Synthesis of non-isocyanate polyurethanes (NIPUs) from α,ω-dihydroxy telechelic PTMC.

hexamethylene diisocyanate, afforded the multiblock copolymer poly(PEG/PPG/PTMC urethane). Such thermogelling copolymers were subsequently used for the sustained delivery of doxorubicin in the effective eradication of cancer cells, thus demonstrating their potential use in chemotherapeutic applications [35].

Recently, we exploited the lately prepared α,ω-dihydroxy telechelic PTMCs [25c] for the synthesis of non-isocyanate polyurethanes (NIPUs) [36]. This involved first the two-step synthesis of the α,ω-di(cyclocarbonate) telechelic PTMC upon chemical modification of the hydroxyl groups of PTMC–$(OH)_2$, followed by the polycondensation reaction with a diamine to afford the desired poly(carbonate urethane) (Scheme 9).

The hydroxy-end functions of HO–PTMC–OH ($\overline{M}n_{SEC}$ = 4950 g mol^{-1}; $Đ_M$ = 1.21) [29a] were reacted with succinic anhydride in the presence of triethylamine and 4-dimethylaminopyridine (DMAP) as catalysts, thereby affording the corresponding PTMC bearing carboxylic end-groups PTMC–$(COOH)_2$ ($\overline{M}n_{SEC}$ = 5300 g mol^{-1}; $Đ_M$ = 1.43) [29e]. Quantitative esterification of these –COOH groups upon reaction with glycerol carbonate afforded the subsequent α,ω-dicyclocarbonate PTMC ($\overline{M}n_{SEC}$ = 5770 g mol^{-1}; $Đ_M$ = 1.31; $Tg \approx -15$ °C) [29f]. This overall procedure was efficient to selectively react with the terminal functions without altering the carbonate backbone chain, as monitored by stepwise ^{1}H NMR analyses [29] and by the MALDI-ToF MS analysis of PTMC–$(OH)_2$ and PTMC–$(cyclocarbonate)_2$. Finally, the ring-opening reaction of both terminal cyclic carbonates of this telechelic macroinitiator with a diamine afforded the poly(carbonate hydroxy urethane)s ($\overline{M}n_{SEC}$ = 68,100 g mol^{-1}; $Đ_M$ = 1.20; $Tg \approx +6$ °C), featuring both primary and secondary hydroxyl groups resulting from both oxygen–acyl opening sites of the unsymmetrical five membered ring cyclocarbonate (Scheme 9). FTIR spectra unambiguously revealed the characteristic vibrations of the urethane and the carbonate groups [37].

Such a synthetic approach to NIPUs from a polycarbonate diol offers several significant advantages over previously established methods for making polyurethanes. First, it does not involve either a toxic isocyanate or a heavy metal (tin) catalyst, an improved important environmental and health factor. More attractively, it allows

tuning the length/molar mass of the soft macromolecular carbonate segments –beyond the shorter length range previously established up to $\overline{M}n \leq 12,000\,g\,mol^{-1}$) and thereby, it enables to modulate the final polyurethane physical properties – and therefore applications – at will. This original strategy appears somewhat "revolutionary" since it provides a smooth access to "greener" polyurethanes without making use of toxic isocyanates [36].

4. Conclusions and outlooks

In this review, the synthesis and versatility of examples of the valuable class of telechelic polyester/polycarbonates prepared from ROP of cyclic esters/carbonates has been highlighted. The major advantage of the borohydride rare earth metal catalysts in the direct access of PCL-, PHB- and PTMC-diols has been unveiled in light of a comprehensive experimental and computational survey. The active borohydride functional group which is prone to reduction of the ketonic carbon atom of the monomer, along with the nature of the ancillary ligand(s) surrounding the metal center, significantly impact the overall ROP mechanism. Other more common and "classical" metal or organic catalyst systems, suitably associating a diol in an iROP procedure, also smoothly afforded such polymer diols.

Although established for quite some time, the concept of chemical modification of a preformed polymer toward the development of block copolymers has been proven to still allow access to original block copolymer architectures. The great opportunity provided by α,ω-dihydroxytelechelic polyesters and polycarbonates is especially expressed in two domains: the ability to prepare analogous linear diblock and triblock PCL/PBLG, PCL/PMMA and PTMC/PLLA copolymers, and the innovative user-friendliness synthesis of non-isocyanate polyurethanes (NIPUs) from dicyclocarbonate telechelic pre-polymers.

With regard to the biocompatibility, (bio)degradability and more importantly to the bioplastic nature of such (co)polymers, the strategies developed in this work, as well as others yet to be envisioned, may reveal a major breakthrough in the near future for the substitution of petrochemical commodity plastics.

Acknowledgements

All co-workers who contributed to this research and whose names appear in the reference section are gratefully acknowledged. Michèle Schappacher is most gratefully acknowledged for her significant contribution to the pioneering investigations on the use of rare earth borohydride catalysts in the ROP of cyclic esters. This research has been financially supported in part by the CNRS, the French Ministry of Higher Education (MESR; Ph.D. grant to I. Palard, M. Le Hellaye), the Laboratoire de Chimie des Polymères Organiques (LCPO, Pessac, France), Total Petrochemicals Co. (Ph.D. grant to M. Helou), Labso Chimie Fine (Blanquefort, France), the Région Bretagne (ACOMB research program) and Rennes Métropole.

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[30] ν_{NH} (3298, 3441/3353 cm^{-1}), ν_{CO} (1651, 1648 cm^{-1}), $\delta_{CO\text{-}NH}$ (1556, 1543 cm^{-1}), and ν_{CO} (1731-PBLG segment and 1727-PCL segment cm^{-1}), characteristic of primary amide and ester groups, respectively.
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